Efficient Templated Synthesis of Donor-Acceptor Rotaxanes using Click Chemistry

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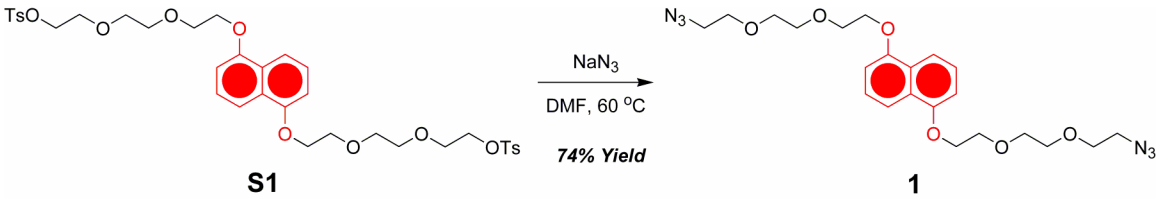
General Methods. All reagents were purchased from commercial suppliers (Aldrich or Fisher) and used without purification. 1,5-Bis[2-(2-(2-(toluene-4-sulfonyl)ethoxy)ethoxy)ethoxy]naphthalene,[1] cyclobis(paraquat-*p*-phenylene),[2] and 4-[bis[4-(*t*-butyl)phenyl][4-(isopropyl)phenyl]methyl]phenol,[3] tris-1,3,5(4′-ethynylphenyl) benzene[4] were prepared using previously published procedures. Thin layer chromatography (TLC) was performed on silica gel 60 F_{254} (E. Merck). Preparative thin layer chromatography (Prep TLC) was performed on glass plates with a 1mm thick layer of silica gel 60 F_{254} (E. Merck). Column chromatography was performed on silica gel 60F (Merck 9385, 0.040-0.063 mm). Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 600 (^{1}H: 600 MHz; ^{13}C: 150 MHz) or 500 (^{1}H: 500 MHz; ^{13}C: 126 MHz) spectrometer. Chemical shifts are reported as parts per million (ppm) downfield from the Me_4Si resonance as the internal standard for both ^{1}H and ^{13}C NMR spectroscopies. Electrospray ionization (ESI) mass spectra were measured on a Finnigan LCQ ion-trap mass spectrometer using 1 : 1 MeCN : H_2O as the mobile phase. High-resolution fast atom bombardment (HR-FAB) mass spectra were obtained on a JEOL JMS-600H high resolution mass spectrometer equipped with a FAB probe. Electrospray ionization mass spectra were obtained on a Finnigan LCQ ion trap mass spectrometer.

Scheme S1. Synthesis of DNP Diazide Derivative **1**.



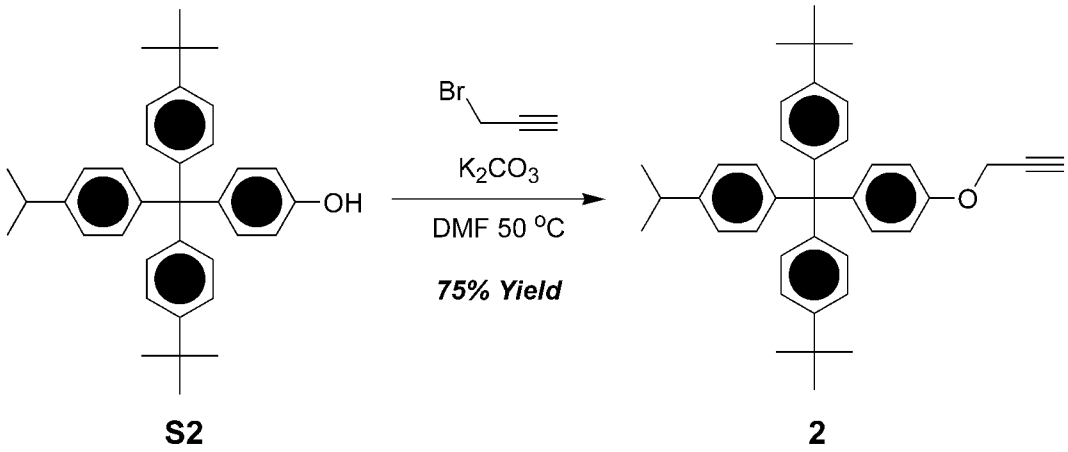
S1 **1**

Preparation of 1,5-Bis[2-(2-(2-(azide)ethoxy)ethoxy)ethoxy]naphthalene 1:

1,5-Bis[2-(2-(2-(toluene-4-sulfonyl)ethoxy)ethoxy)ethoxy]naphthalene[1] (**S1,** 0.200 g, 0.273 mmol) and sodium azide (0.355 g, 5.458 mmol) were dissolved in DMF (2.7 mL) and heated to 60 ^{o}C for 12h. The crude reaction mixture was partitioned between 100 mL of water and CH_2Cl_2, and the aqueous phase was washed with CH_2Cl_2 (3 x 50 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), and the solvent evaporated. The crude product was chromatographed (SiO_2, 7:3 CH_2Cl_2 : Et_2O eluent) to

give 96 mg (74.4% yield) of **1** as a pale yellow solid. **1**: ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ 7.86 (d, ^{3}J (H,H) = 9 Hz, 2H, DNP aryl -H *p*-O), 7.35 (t, ^{3}J (H,H) = 9 Hz, 2H, DNP aryl -H *m*-O), 6.84 (d, ^{3}J (H,H) = 8 Hz, 2H, DNP aryl -H *o*-O), 4.31 (t, ^{3}J (H,H) = 5 Hz, 4H, DNP-OCH_2), 4.00 (t, ^{3}J (H,H) = 5 Hz, 4H), 3.82 (t, ^{3}J (H,H) = 9 Hz, 4H), 3.71 (m, 8H), 3.37 (t, ^{3}J (H,H) = 5 Hz, 4H, CH_2N_3); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ^{o}C): δ 154.2, 126.7, 125.0, 114.5, 105.6, 71.0, 70.7, 70.0, 69.8, 67.8, 50.6; HRMS (FAB): Calcd for $C_{22}H_{30}N_6O_6$ *m/z* = 474.2227. Found *m/z* = 474.2226.

Scheme S2. Synthesis of Alkyne Functionalized Stopper **2**.



Preparation of 4-[bis[4-(*t*-butyl)phenyl][4-(isopropyl)phenyl]methyl]phenyl propargyl ether (2):

Tetraarylmethane **S2** (4-[bis[4-(*t*-butyl)phenyl][4-(isopropyl)phenyl]methyl]phenol,[3] 0.750 g, 1.528 mmol) and K_2CO_3 (0.634 g, 4.585 mmol) were suspended in DMF (7.6 mL). Propargyl bromide (0.6 g of an 80 wt% solution in xylenes, 3.47 mmol) was added and the solution was heated to 50 ^{o}C for 12h. The reaction mixture was poured in 75 mL of EtOAc and was washed with 1M $NaHSO_4$ (75 mL), H_2O (2 x 75 mL), brine (75 mL), and dried ($MgSO_4$). The solution was evaporated onto silica gel, loaded onto a silica gel column, and chromatographed using 1:9 EtOAc:hexanes as the eluent to obtain 0.602 g (75% yield) of **2** as a white solid. **2**: ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C, TMS): 7.22 (d, ^{2}J(H,H) = 9 Hz, 4H, Ar-H *ortho*-tBu), 7.12 (d, ^{2}J(H,H) = 7 Hz, 2H, Ar-H, Ar-H *ortho*-iPr), 7.07 (m, 8H, all meta Ar-H), 6.85 (d, ^{2}J(H,H) = 6 Hz, 2H, Ar-H *ortho*-O), 4.66 (d, ^{2}J(H,H) = 2 Hz, -O-CH_2-), 2.88 (septet, ^{2}J(H,H) = 7 Hz, 1H, -$CH(CH_3)_2$), 2.52 (t, ^{2}J(H,H)

= 2 Hz, 1H, CCH), 1.30 (s, 18H, tBu), 1.24 (d, ^{2}J(H,H) = 7 Hz, 6H, iPr); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.4, 148.2, 146.0, 144.4, 144.0, 140.4, 132.2, 130.9, 130.6, 125.1, 124.0, 113.2, 78.7, 75.3, 63.1, 55.7, 34.2, 33.4, 31.3, 23.9; HRMS (FAB): Calcd for $C_{39}H_{45}O$ *m/z* = 529.3470. Found *m/z* = 529.3449.

Preparation of the [2]Rotaxane 3 · 4PF$_6$:

Diazide DNP derivative **1** (0.0070 g, 0.015 mmol), CBPQT^{4+} (0.017 g, 0.015 mmol), and the alkyne functionalized stopper **2** (0.016 g, 0.031 mmol) were dissolved in DMF (0.160 mL) at -10 ^{o}C, forming a deep red solution. Stock solutions of $CuSO_4 \cdot 5H_2O$ in DMF (20 μL, 0.074M) and ascorbic acid in DMF (20 μL, 0.148M) were added. The solution was stirred at -10 ^{o}C for 24 h, at which time the solvent was evaporated. The red solid was redissolved in Me_2CO and the [2]rotaxane was purified by preparative TLC using a 1% w/v NH_4PF_6 solution in Me_2CO as the mobile phase. The rotaxane product was recovered from the silica gel by washing with an excess of eluent solution. The Me_2CO was concentrated to a minimum volume, and the product was precipitated from this solution through the addition of an excess of cold water. The click [2]rotaxane **3** · 4PF$_6$ was isolated as a purple solid (0.033 g, 84% yield). **3** · 4PF$_6$**:** ^{1}H NMR (500 MHz, CD_3COCD_3, 52 ^{o}C): δ 9.21 (br s, 8H, α-CBPQT^{4+}), 8.29 (s, 8H, β-CBPQT^{4+}), 8.02 (s, 2H, triazole-H), 7.75 (br s, 8H, aryl-CBPQT^{4+}), 7.29 (d, , ^{3}J (H,H) = 7 Hz, 8H, stopper aryl-H *o*-tBu), 7.11 (m, 20H, stopper - all meta Ar-H plus *o*-iPr aryl -H), 6.84 (d, ^{3}J (H,H) = 9 Hz , 4H, stopper aryl -H *o*-O), 6.49 (d, ^{3}J (H,H) = 8 Hz, 2H, DNP *o*-O), 6.26 (t, ^{3}J (H,H) = 8 Hz, 2H, DNP- *m*-O), 6.02 (br s, 8H, CBPQT^{4+} benzyl H), 4.97 (s, 4H, stopper-OCH_2), 4.61 (t, ^{3}J (H,H) = 5 Hz, 4H), 4.50 (br m, 4H), 4.30 (br m, 4H), 4.15 (t, ^{3}J (H,H) = 5 Hz, 4H), 4.09 (br m, 4H), 4.00 (br m, 4H), 2.89 (septet, ^{3}J (H,H) = 7 Hz, 2H, stopper iPr H), 2.80 (d, ^{3}J (H,H) = 8 Hz, 2H, DNP *p*-O), 1.31 (s, 36H, tBu), 1.23 (d, ^{3}J (H,H) = 7 Hz, 12H, iPr CH_3); ^{13}C NMR (125 MHz, CD_3COCD_3, 52 ^{o}C): 149.6, 147.3, 146.7, 145.8, 145.4, 137.9, 133.1, 132.6, 131.9, 131.7, 129.3, 126.3, 125.8, 125.2, 114.6, 110.0, 105.9, 72.1, 71.8, 71.1, 70.5, 69.3, 66.6, 64.3, 62.6, 35.0, 34.3, 31.8, 24.3; MS (ESI, 1:1 MeCN:H_2O, 0.1% AcOH): Found 1170.9 $(M - 2PF_6)^{2+}$, 723.3 $(M - 3PF_6)^{3+}$, 512.9 $(M - 4PF_6)^{4+}$.

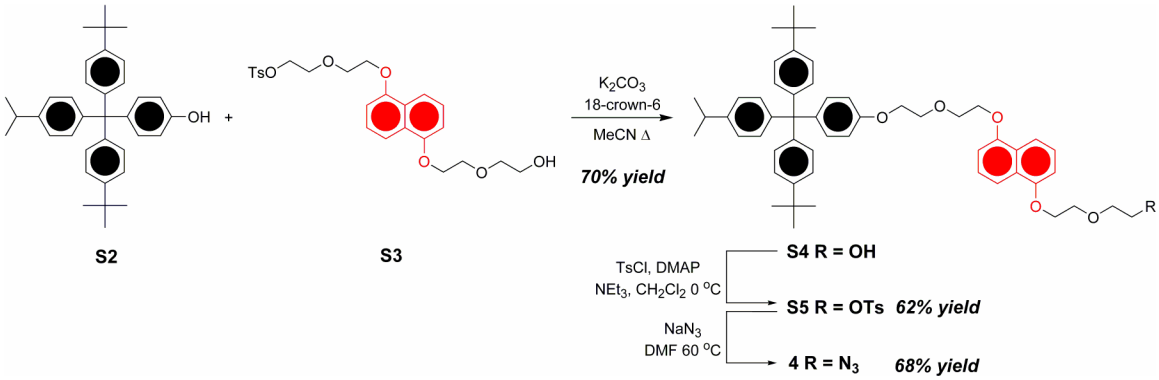
General Click Chemistry Procedure for the Synthesis of High Order Rotaxanes and Preparation of [3]Rotaxane 6 · $8PF_6$:

DNP derivative **4** (0.013 g, 0.0155 mmol, 1.05 eq. per alkyne), $CBPQT^{4+}$ (0.0195 g, 0.0178 mmol, 1.2 eq. per alkyne), and the dialkyne functionalized tetraarylmethane **5** (0.0040 g, 0.0074 mmol) were dissolved in DMF (0.090 mL) at –10 °C, forming a deep red solution. Stock solutions of $CuSO_4 \cdot 5H_2O$ in DMF (20 μL, 0.036M, 0.05 eq per alkyne) and ascorbic acid in DMF (20 μL, 0.072M, 0.1 eq. per alkyne) were added. The solution was stirred at –10 °C for 24 h, at which time the solvent was evaporated. The red solid was redissolved in Me_2CO and the product [2]rotaxane was purified by preparative TLC using a 2% w/v NH_4PF_6 solution in Me_2CO as the mobile phase. The rotaxane product was recovered from the silica gel by washing with an excess of Me_2CO / NH_4PF_6 solution. The Me_2CO was concentrated to a minimum volume, and the product was precipitated from this solution through the addition of an excess of cold water. The click [3]rotaxane **6** · $8PF_6$ (0.033 g, 84% yield) was isolated by filtration as a purple solid and dried under high vacuum overnight. **6** · $8PF_6$**:** ^{1}H NMR (500 MHz, CD_3CN, 75 °C): δ 8.77 (br s, 16H, α-$CBPQT^{4+}$), 8.07 (s, 2H, triazole-H), 7.99 (s, 16H, β-$CBPQT^{4+}$), 7.30 (m, 28H, aryl-$CBPQT^{4+}$, all stopper aryl-H *o*-tBu), 7.10 (m, 28H, stopper m- aryl -H, stopper aryl -H *o*-iPr), 6.86 (m, 8H, stopper aryl -H *o*-O), 6.41 (d, ^3J (H,H) = 8 Hz, 2H, DNP *o*-O), 6.37 (d, ^3J (H,H) = 8 Hz, 2H, DNP *o*-O), 6.01 (m, 4H, DNP- *m*-O), 5.79 (d, ^2J (H,H) = 13 Hz, 8H, $CBPQT^{4+}$ benzyl H), 5.79 (d, ^2J (H,H) = 13 Hz, 8H, $CBPQT^{4+}$ benzyl H), 5.11 (s, 4H, OCH_2-triazole), 4.83 (t, ^3J (H,H) = 5 Hz, 4H, triazole – CH_2), 4.46 (br m, 8H), 4.30 (br m, 12H), 4.25 (m, 8H), 2.88 (septet, ^3J (H,H) = 7 Hz, 2H, stopper iPr H), 2.56 (d, ^3J (H,H) = 8 Hz, 2H, DNP *p*-O), 2.55 (d, ^3J (H,H) = 8 Hz, 2H, DNP *p*-O), 1.31 (s, 18H, central tBu), 1.29 (s, 36H, external tBu), 1.22 (d, ^3J (H,H) = 7 Hz, 12H, stopper iPr); ^{13}C MS (ESI, 1:1 MeCN:H_2O, 0.1% AcOH): δ 156.2, 156.1, 150.9, 148.5, 148.4, 146.2, 145.2, 144.7, 144.3, 144.3, 143.8, 140.1, 140.0, 136.4, 131.8, 131.6, 131.2, 130.3, 130.0, 128.0, 127.9, 126.1 125.4, 124.6, 124.3, 124.2, 124.2, 113.5, 113.4, 108.2, 104.4, 104.3, 70.4, 69.8, 69.6, 68.2, 68.0, 65.0, 62.9, 62.6, 61.1, 50.5, 33.8, 33.8, 33.1, 30.5, 30.4, 23.1; Found 1324.6 $(M - 3PF_6)^{3+}$, 957.3 $(M - 4PF_6)^{4+}$, 736.9 $(M - 5PF_6)^{5+}$, 589.9 $(M - 6PF_6)^{6+}$, 484.9 $(M - 7PF_6)^{7+}$.

Preparation of [4]Rotaxane 8 · 12PF$_6$:

The above procedure was followed using tris-1,3,5(4′-ethynylphenyl)benzene **7**[5] (0.0040 g, 0.011 mmol) as the alkyne containing component. Preparative TLC as described above provided the [4]rotaxane **8** · 12PF$_6$ (47.5 mg, 72% yield) as a purple solid. **8** · 12PF$_6$**:** ^{1}H NMR (500 MHz, CD_3COCD_3, 52 ^{o}C): δ 9.17 (br s, 24H, α-CBPQT^{4+}), 8.61 (s, 3H, triazole-H), 8.28 (s, 24H, β-CBPQT^{4+}), 7.79 (m, 39H, aryl-CBPQT^{4+}, all central unit Ar-H), 7.26 (d, , ^3J (H,H) = 7 Hz, 12H, stopper aryl -H *o*-tBu), 7.07 (m, 30H, stopper - all meta Ar-H plus *o*-iPr aryl -H), 6.88 (d, ^3J (H,H) = 9 Hz , 6H, stopper aryl -H *o*-O), 6.49 (d, ^3J (H,H) = 8 Hz, 6H, DNP *o*-O), 6.22 (overlapping t, ^3J (H,H) = 8 Hz, 6H, both DNP-*m*-O), 6.03 (br m, 24H, CBPQT^{4+} benzyl H), 4.00 (t, ^3J (H,H) = 8 Hz, 6H, stopper-OCH_2), 4.55 (m, 12H), 4.50 (m, 12H), 4.43 (m, 12H), 4.32 (t, ^3J (H,H) = 5 Hz, 6H, triazole-NCH_2), 2.86 (septet, ^3J (H,H) = 7 Hz, 3H, stopper iPr H), 2.55 (br s, 3H, DNP *p*-O), 1.28 (s, 54H, tBu), 1.20 (d, ^3J (H,H) = 7 Hz, 12H, iPr CH_3); ^{13}C NMR (125 MHz, CD_3COCD_3, 25 ^{o}C):156.2, 150.8, 148.4, 147.2, 146.2, 145.2, 144.7, 144.3, 143.6, 141.4, 140.2, 140.0, 136.3, 131.8, 131.2, 130.3, 130.0, 127.9, 127.9, 127.7, 126.2, 125.7, 125.4, 124.6, 124.3, 124.2, 121.5, 113.4, 108.2, 104.4, 104.2, 70.35, 69.9, 69.7, 68.1, 68.0, 65.0, 62.9,50.5, 33.8, 33.1, 30.4, 23.1; MS (ESI, 1:1 MeCN:H_2O, 0.1% AcOH): Found 1915.2 (M – 3PF$_6$)$^{3+}$, 1400.3 (M – 4PF$_6$)$^{4+}$, 1091.3 (M – 5PF$_6$)$^{5+}$, 885.3 (M – 6PF$_6$)$^{6+}$, 738.1 (M – 7PF$_6$)$^{7+}$, 627.7 (M – 8PF$_6$)$^{8+}$, 541.8 (M – 9PF$_6$)$^{9+}$.

Scheme S3. Preparation of DNP Azide Derivative **4**.



Preparation of Stopper-DNP-OH S4. Tetraarylmethane **S2** (1.500 g, 3.057 mmol), dioxynaphthalene monotosylate derivative **S3** (1.799 g, 3.668 mmol),[4] K_2CO_3 (1.690 g,

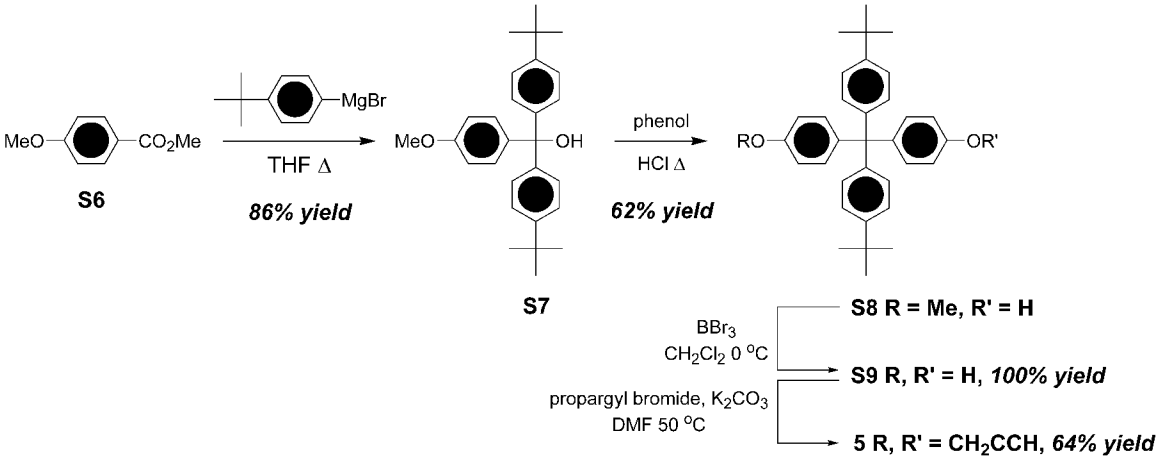
12.23 mmol), and [18]crown-6 (0.040 g, 0.153 mmol) were taken up in MeCN (30 mL). The heterogeneous solution was refluxed with vigorous stirring for 12 h. The reaction mixture was filtered through celite and the solvent was evaporated. Flash chromatography of the crude product (SiO_2, 85:15 CH_2Cl_2 : hexanes) yielded 1.725 g (70% yield) of the alkylation product **S4** as an amorphous white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ 7.88 (d, ^3J (H,H) = 9 Hz, 1H, DNP *p*-O), 7.86 (d, ^3J (H,H) = 9 Hz, 1H, DNP aryl -H *p*-O), 7.32 (m, 2H, DNP aryl -H *m*-O), 7.23 (m, 4H, stopper aryl -H *o*-tBu), 7.09 (m, 10H, stopper all meta Ar-H and *o*-iPr), 6.85 (d, ^3J (H,H) = 8 Hz, 1H, DNP aryl -H *o*-O), 6.84 (d, ^3J (H,H) = 8 Hz, 1H, DNP aryl -H *o*-O), 6.80 (d, ^3J (H,H) = 9 Hz, 2H, stopper aryl -H *o*-O), 4.31 (m, 4H, both DNP-OCH_2), 4.16 (t, ^3J (H,H) = 5 Hz, 2H, stopper -OCH_2), 4.07 (t, ^3J (H,H) = 5 Hz, 2H, stopper -$OCH_2C\mathit{H_2}$), 4.00 (m, 4H, both DNP-$OCH_2C\mathit{H_2}$), 3.78 (m, 2H, $HOCH_2C\mathit{H_2}$), 3.75 (m, 2H, $HOC\mathit{H_2}$), 2.88 (septet, ^3J (H,H) = 7 Hz, 1H, iPr-H), 1.31 (s, 18H, t-Bu), 1.24 (d, ^3J (H,H) = 7 Hz, 6H, iPr –CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ^{o}C): δ 156.4, 154.3, 154.1, 148.2, 145.9, 144.5, 144.0, 139.7, 132.1, 130.9, 130.6, 128.9, 128.8, 126.7, 126.6, 125.1, 125.1, 125.0, 124.0, 114.7, 114.4, 113.0, 105.7, 72.5, 70.0, 69.9, 69.7, 67.9, 67.8, 67.2, 63.0, 61.8, 34.2, 33.4, 23.9; HRMS (FAB): Calcd for $C_{54}H_{64}O_6$ *m/z* = 808.4703. Found *m/z* = 808.4701

Preparation of Stopper-DNP-OTs S5: S4 (0.300 g, 0371 mmol), DMAP (0.005 g, 0.037 mmol), and triethylamine (0.261 mL, 1.854 mmol) were dissolved in CH_2Cl_2 (3.7 mL). The solution was cooled to 0 ^{o}C, and *p*-toluenesulfonyl chloride (0.085 g, 0.445 mmol) was added. The solution was allowed to warm slowly to RT while stirring for 12 h. The reaction mixture was diluted into CH_2Cl_2 (50 mL), washed with H_2O (2 x 50 mL), saturated NH_4Cl (2 x 50 mL), brine (1 x 50 mL), dried ($MgSO_4$), filtered, and the solvent evaporated. The crude product was passed through a short plug of SiO_2 in CH_2Cl_2 to obtain 0.221 g (61.9% yield) of the pure tosylated product **S5**. **S5:** ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ 7.83 (d, ^3J (H,H) = 9 Hz, 1H, DNP *p*-O), 7.79 (d, ^3J (H,H) = 9 Hz, 1H, DNP aryl -H *p*-O), 7.78 (d, ^3J (H,H) = 8 Hz, 2H, tosylate aryl -H *o*-S), 7.30 (m, 2H, DNP aryl -H *m*-O), 7.23 (m, 4H, stopper aryl -H *o*-tBu), 7.08 (m, 10H, stopper all meta Ar-H and *o*-iPr), 6.85 (d, ^3J (H,H) = 8 Hz, 1H, DNP aryl -H *o*-O), 6.80 (d, ^3J (H,H) = 9 Hz, 2H, stopper aryl -H *o*-O), 6.78 (d, ^3J (H,H) = 8 Hz, 1H, DNP aryl -H *o*-O), 4.32

(t, ^3J (H,H) = 5 Hz, 2H), 4.19 (m, 6H), 4.07 (t, ^3J (H,H) = 5 Hz, 2H), 3.99 (t, ^3J (H,H) = 5 Hz, 2H), 3.91 (t, ^3J (H,H) = 5 Hz, 2H), 3.83 (t, ^3J (H,H) = 5 Hz, 2H), 2.87 (septet, ^3J (H,H) = 7 Hz, 1H, iPr-H), 2.35 (s, 3H, OTs -CH_3), 1.29 (s, 18H, t-Bu), 1.24 (d, ^3J (H,H) = 7 Hz, 6H, iPr –CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ^{o}C): δ 156.4, 154.2, 154.0, 148.2, 145.9, 144.7, 144.5, 144.1, 139.7, 132.1, 130.9, 130.6, 129.7, 128.9, 127.9, 126.7, 126.6, 125.1, 125.0, 124.0, 114.7, 114.4, 113.0, 105.7, 105.6, 70.0, 69.8, 69.3, 68.9, 67.9, 67.8, 67.2, 63.0, 34.2, 33.3, 31.3, 29.6, 23.9, 21.5. HRMS (FAB): Calcd for $C_{61}H_{70}O_8S$ *m/z* = 962.4791. Found *m/z* = 962.4833.

Preparation of Stopper-DNP-N3 (4): S5 (0.275 g, 0.285 mmol) and sodium azide (0.186 g, 2.855 mmol) were stirred in DMF (3.81 mL) at 50 ^{o}C for 6 h. The reaction mixture was filtered through celite and the solvent was evaporated. The resulting solid was sonicated in CH_2Cl_2 and soluble fractions chromatographed (SiO_2, 8:2 CH_2Cl_2 eluent) to yield 0.170 g (68% yield) of **4** as an amourphous white powder. **4**: ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ 7.89 (d, ^3J (H,H) = 8 Hz, 1H, DNP *p*-O), 7.87 (d, ^3J (H,H) = 8 Hz, 1H, DNP aryl -H *p*-O), 7.34 (m, 2H, DNP aryl -H *m*-O), 7.23 (m, 4H, stopper aryl -H *o*-tBu), 7.09 (m, 10H, stopper all meta Ar-H and *o*-iPr), 6.85 (d, ^3J (H,H) = 8 Hz, 1H, DNP aryl -H *o*-O), 6.84 (d, ^3J (H,H) = 8 Hz, 1H, DNP aryl -H *o*-O), 6.80 (d, ^3J (H,H) = 9 Hz, 2H, stopper aryl -H *o*-O), 4.32 (m, 4H), 4.16 (t, ^3J (H,H) = 5 Hz, 2H), 4.07 (t, ^3J (H,H) = 5 Hz, 2H), 4.01 (m, 4H), 3.84 (t, ^3J (H,H) = 5 Hz, 2H), 3.44 (t, ^3J (H,H) = 5 Hz, 2H, -CH_2N_3), 2.88 (septet, ^3J (H,H) = 7 Hz, 1H, iPr-H), 1.30 (s, 18H, t-Bu), 1.24 (d, ^3J (H,H) = 7 Hz, 6H, iPr –CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ^{o}C): δ 156.5, 154.2, 154.1, 148.2, 145.9, 144.5, 144.0, 139.7, 132.1, 130.9, 130.6, 126.7, 126.6, 125.1, 125.1, 125.0, 124.0, 114.7, 114.5, 113.0, 105.6, 70.3, 70.0, 69.9, 69.8, 67.9, 67.2, 63.0, 50.7, 34.2, 33.3, 31.3, 23.9; HRMS (FAB): Calcd for $C_{54}H_{63}N_3O_5$ *m/z* = 873.4768. Found *m/z* = 873.4736.

Scheme S4. Synthesis of dialkyne stopper derivative **5**.



Preparation of Trityl Alcohol S7. 4-*t*-Butylphenyl bromide (24.5 mL, 30.1 g, 141.4 mmol) was added slowly to freshly cleaned magnesium turnings (3.50 g, 144 mmol; cleaned by sonication in Et_2O) in THF (65 mL) under an Ar atmosphere. The solution was heated under reflux for 4 h until the solid Mg had disappeared. The Grignard reagent was cooled down to 0 ^oC and a solution of methyl 4-methoxybenzoate (**S6**, 10.00 g, 60.2 mmol) in the minimum amount of THF was added by cannula transfer. The mixture was heated under reflux for 1 h, then was taken up in CH_2Cl_2 (100 mL), washed with sat. NH_4Cl (3 x 100 mL) and brine, dried ($MgSO_4$), and the solvent evaporated. The crude product was recrystallized from hexanes to yield 20.8 g (86% yield) of **S7** as white crystals. **S7**: ^1H NMR (500 MHz, $CDCl_3$, 25 ^oC): δ 7.33-7.31 (m, 4 H, H-Ar), 7.21-7.18 (m, 6 H, H-Ar), 6.84 (d, ^3J (H,H) = 9 Hz, 2 H, H-Ar), 3.80 (s, 3 H, -OCH_3), 1.321 (s, 18 H, -CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.4, 149.8, 144.1, 139.5, 129.0, 127.4, 124.6, 113.0, 81.3, 55.1, 34.3, 31.3; Anal. C: 83.74, H: 8.18 (calcd C: 83.54, H: 8.51). HRMS (FAB): Calcd for $C_{28}H_{34}O_2$ *m/z* = 402.2559. Found *m/z* = 402.2567.

Preparation of Tetraarylmethane Alcohol S8. Trityl alcohol **S7** (10.00 g, 24.2 mmol) and phenol (45.4 g, 483 mmol) were mixed neat and heated to 80 ^oC until the phenol melted. Concentrated HCl (1.1 mL) was added and the solution was heated to 100 ^oC for 5 h. The reaction mixture was taken up in PhMe, washed with aqueous 0.5 M NaOH (7 x 75 mL), and dried ($MgSO_4$), and the solvent evaporated to give the crude product as a yellow oil. Chromatography (silica gel, 25% hexanes in CH_2Cl_2) afforded 6.06 g (62%

yield) of **S8** as a white powder. **S8**: ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ 7.24-7.22 (m, 4 H, H-Ar), 7.10-7.04 (m, 8 H, H-Ar), 6.77 (d, ^{3}J (H,H) = 9 Hz, 2 H, H-Ar), 6.70 (d, ^{3}J (H,H) = 9 Hz, 2 H, H-Ar), 4.63 (s, 1 H, -OH), 3.79 (s, 3 H, -OCH_3), 1.30 (s, 18 H, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.3, 153.3, 148.4, 144.2, 139.9, 139.7, 132.4, 132.2, 130.6, 129.1, 124.1, 114.0, 112.5, 62.8, 55.2, 34.3, 31.4; Anal. C: 84.89, H: 8.15 (calcd C: 85.31, H: 8.00). HRMS (FAB): Calcd for $C_{34}H_{38}O_2$ *m/z* = 478.2872. Found *m/z* = 478.2886.

Preparation of Tetraarylmethane Diol S9. **A** 1M solution of BBr_3 in CH_2Cl_2 (23.0 mL, 23.0 mmol) was added dropwise to a solution of methyl aryl ether **S8** (5.00 g, 10.4 mmol) in CH_2Cl_2 (350 mL) at 0 ºC. The reaction mixture was warmed up to room temperature and stirred for 36 h under Ar. MeOH (5 mL) and then H_2O (200 mL) were added to quench the reaction. The organic layer was separated and collected. The aqueous layer was washed with CH_2Cl_2 (3 x 200 mL) and the combined organic layers were dried ($MgSO_4$). Removal of the solvent *in vacuo* afforded 4.85 g (100% yield) of **S9** as an orange powder requiring no further purification. **S9**: ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C): δ 7.23 (d, ^{3}J (H,H) = 9 Hz, 4 H, H-Ar), 7.07 (d, ^{3}J (H,H) = 9 Hz, 4 H, H-Ar), 7.04 (d, ^{3}J (H,H) = 9 Hz, 4 H, H-Ar), 6.70 (d, ^{3}J (H,H) = 9 Hz, 4 H, H-Ar), 1.30 (s, 18 H, -CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.1, 148.3, 144.0, 139.8, 132.3, 130.5, 124.0, 113.9, 62.7, 34.2, 31.3; HRMS (FAB): Calcd for $C_{33}H_{36}O_2$ *m/z* = 464.2715. Found *m/z* = 464.2721.

Preparation of Diacetylene 5. Propargyl bromide (80% w/w solution in xylenes, 4.80 g, 32.3 mmol) and K_2CO_3 (2.68 g, 19.4 mmol) were added to a solution of diol **S9** (1.50 g, 3.23 mmol) in DMF (20 mL) was added. The reaction mixture was heated to 50 ºC and stirred for 40 h under Ar. The reaction was taken up in EtOAc (150 mL), washed with 1 M $NaHSO_4$ (1 x 150 mL), H_2O (2 x 100 mL), and brine (2 x 100 mL), dried ($MgSO_4$), and evaporated onto silica gel. Chromatography (silica gel, 10% EtOAc in hexanes) afforded 1.12 g (64% yield) of **5**. **5**: ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C): δ 7.24 (d, ^{3}J (H,H) = 9 Hz, 4 H, H-Ar), 7.10 (d, ^{3}J (H,H) = 9 Hz, 4 H, H-Ar), 7.07 (d, ^{3}J (H,H) = 9 Hz, 4 H, H-Ar), 6.85 (d, ^{3}J (H,H) = 9 Hz, 4 H, H-Ar), 4.66 (d, ^{4}J (H,H) = 2 Hz, 4 H, -

CH_2-), 2.52 (t, ^4J (H,H) = 2 Hz, 2 H, H-acetylene), 1.30 (s, 18 H, -CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.4, 148.3, 143.9, 140.3, 132.0, 130.5, 124.0, 113.3, 78.7, 75.3, 62.7, 55.7, 34.2, 31.3; HRMS (FAB): Calcd for $C_{39}H_{40}O_2$ *m/z* = 540.3028. Found *m/z* = 540.3042.

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